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(54) Title: SELF-DESTRUCTING FILTER CAKE

Dissolution of 1 mole Calcite at 82 C
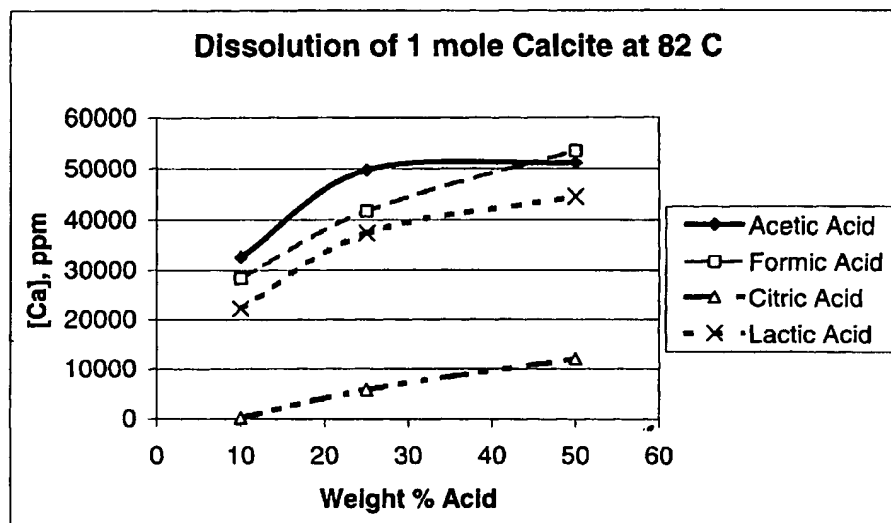
(57) Abstract: A composition and method are given for self-destructive fluid loss additives and filter cakes in wellbores and subterranean formations. The fluid loss additives and filter cakes are formed from a mixture of particulate solid acid-precursors, such as a polylactic acid or a polyglycolic acid, and particulate solid acid-reactive materials, such as magnesium oxide or calcium carbonate. In the presence of water, the solid acid-precursors hydrolyze and dissolve, generating acids that then dissolve the solid acid-reactive materials. The composition is used in oilfield treatments such as drilling, completion and stimulation where it disappears when it is no longer needed without the use of mechanical means or injection of additional fluids.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SELF-DESTRUCTING FILTER CAKE

Background of the Invention

This invention relates to a composition and method for generating self-destructing
filter cakes in wellbores and in subterranean formations. More particularly it relates to a
composition and method for injection of solids-containing fluids that form filter cakes in
which acids are generated after the filter cakes have been placed. Finally, it relates to using
the composition and method in oilfield applications.

There are many oilfield applications in which filter cakes are needed in the wellbore,
in the near-wellbore region or in one or more strata of the formation. Such applications are
those in which without a filter cake fluid would leak off into porous rock at an undesirable
rate during a well treatment. Such treatments include drilling, drill-in, completion,
stimulation (for example, hydraulic fracturing or matrix dissolution), sand control (for
example gravel packing, frac-packing, and sand consolidation), diversion, scale control,
water control, and others. Typically, after these treatments have been completed the
continued presence of the filter cake is undesirable or unacceptable.

Solid, insoluble, materials (that may be called fluid loss additives and filter cake
components) are typically added to the fluids used in these treatments to form the filter cakes,
although sometimes soluble (or at least highly dispersed) components of the fluids (such as
polymers or crosslinked polymers) may form the filter cakes. Removal of the filter cake is
typically accomplished either by a mechanical means (scraping, jetting, or the like), by
subsequent addition of a fluid containing an agent (such as an acid, a base, or an enzyme) that
dissolves at least a portion of the filter cake, or by manipulation of the physical state of the
filter cake (by emulsion inversion, for example). These removal methods usually require a
tool or addition of another fluid (for example to change the pH or to add a chemical). This
can sometimes be done in the wellbore but normally cannot be done in a proppant or gravel
pack. Sometimes the operator may rely on the flow of produced fluids (which will be in the
opposite direction from the flow of the fluid when the filter cake was laid down) to loosen the
filter cake or to dissolve the filter cake (for example if it is a soluble salt). However, these

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methods require fluid flow and often result in slow or incomplete filter cake removal. Sometimes a breaker can be incorporated in the filter cake but these must normally be delayed (for example by esterification or encapsulation) and they are often expensive and/or difficult to place and/or difficult to trigger.

5   There is a need for a new composition and method in which a filter cake is formed from at least two components, one of which slowly reacts with water, and the second of which reacts with a reaction product of the first to destroy the filter cake spontaneously.

Summary of the Invention

10   One embodiment is an oilfield treatment composition including first a solid that is one or more of lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures of the
15   preceding, and second a solid that reacts with an acid. We will call the former a "solid acid-precursor" and the latter a "solid acid-reactive material". In another embodiment, the solid acid-reactive material is capable of at least partially dissolving in an aqueous fluid. In yet another embodiment, the solid acid-reactive material promotes the formation of acid from the solid acid-precursor. In another embodiment of the Invention, solid particles or fibers or
20   other shapes of the solid acid-precursors of the Invention are formed that include other materials, useful in oilfield treatments, for example solid acid-reactive materials such as calcium carbonate, aluminum hydroxide, magnesium oxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and sodium calcium magnesium polyphosphate glass. The solid acid-precursor in the oilfield
25   treatment composition, including an embodiment in which it is mixed with or contains other materials, may be coated or encapsulated.

Methods of the Invention include incorporation of solid acid-precursors and acid-reactive materials in treatment fluids to form filter cakes in drilling, drill-in and completion treatments, in hydraulic fracturing treatments, in diversion treatments, in scale control
30   treatments, in water control treatments, in matrix dissolution treatments, in sand consolidation

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treatments, in frac-packing treatments, and in gravel packing treatments such that delayed

acid generation occurs to delay at least part of the filter cake after the drilling, completion,

fracturing, diversion or sand control treatment. Other embodiments include using the solid

acid-precursors and the solid acid-reactive materials in combination as components of fluid

5   loss additives that generate acid, after their use, to destroy some or all of the fluid loss

additive. Other embodiments include using the solid acid-precursors and solid acid-reactive

materials in combination as components of drilling fluids, drill-in fluids, completion fluids,

diversion fluids, and stimulation fluids such that the solid acid-precursors form part of the

filter cake and then form acids in the filter cake to react with the solid acid-reactive materials

10   to destroy some or all of the filter cake after a suitable delay.

Brief Description of the Drawings

Figure 1 shows the ability of various organic acids to dissolve calcite.

15   ## Detailed Description of the Invention

Excellent sources of acid that can be generated downhole when and where it is needed

are solid cyclic dimers, or solid polymers, of certain organic acids, that hydrolyze under

known and controllable conditions of temperature, time and pH to form the organic acids.

We will call these solid materials "acid-precursors" and we will call the formation of acid

20   downhole "delayed acid generation". One example of a suitable solid acid-precursor is the

solid cyclic dimer of lactic acid (known as "lactide"), which has a melting point of 95 to 125

°C, (depending upon the optical activity). Another is a polymer of lactic acid, (sometimes

called a polylactic acid (or "PLA"), or a polylactate, or a polylactide). Another example is

the solid cyclic dimer of gylycolic acid (known as "glycolide"), which has a melting point of

25   about 86 °C. Yet another example is a polymer of glycolic acid (hydroxyacetic acid), also

known as polyglycolic acid ("PGA"), or polyglycolide. Another example is a copolymer of

lactic acid and glycolic acid. These polymers and copolymers are polyesters.

Cargill Dow, Minnetonka, MN, USA, produces the solid cyclic lactic acid dimer called "lactide" and from it produces lactic acid polymers, or polylactates, with varying molecular weights and degrees of crystallinity, under the generic trade name NATUREWORKS™ PLA. The PLA's currently available from Cargill Dow have molecular weights of up to about 100,000, although any polylactide (made by any process by any manufacturer) and any molecular weight material of any degree of crystallinity may be used in the embodiments of the Invention. The PLA polymers are solids at room temperature and are hydrolyzed by water to form lactic acid. Those available from Cargill Dow typically have crystalline melt temperatures of from about 120 to about 170 °C, but others are obtainable. Poly(d,l-lactide) is available from Bio-Invigor, Beijing and Taiwan, with molecular weights of up to 500,000. Bio-Invigor also supplies polyglycolic acid (also known as polyglycolide) and various copolymers of lactic acid and glycolic acid, often called "polyglactin" or poly(lactide-co-glycolide). The rates of the hydrolysis reactions of all these materials are governed by the molecular weight, the crystallinity (the ratio of crystalline to amorphous material), the physical form (size and shape of the solid), and in the case of polylactide, the amounts of the two optical isomers. (The naturally occurring l-lactide forms partially crystalline polymers; synthetic dl-lactide forms amorphous polymers.) Amorphous regions are more susceptible to hydrolysis than crystalline regions. Lower molecular weight, less crystallinity and greater surface-to-mass ratio all result in faster hydrolysis. Hydrolysis is accelerated by increasing the temperature, by adding acid or base, or by adding a material that reacts with the hydrolysis product(s).

Homopolymers can be more crystalline; copolymers tend to be amorphous unless they are block copolymers. The extent of the crystallinity can be controlled by the manufacturing method for homopolymers and by the manufacturing method and the ratio and distribution of lactide and glycolide for the copolymers. Polyglycolide can be made in a porous form. Some of the polymers dissolve very slowly in water before they hydrolyze.

Other materials suitable as solid acid-precursors are all those polymers of hydroxyacetic acid (glycolic acid) with itself or other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties described in U.S. Patent Nos. 4, 848,467; 4,957,165; and 4,986,355.

In many oilfield applications, fluid loss additives and filter cakes are needed during a treatment, but after the treatment it is desirable that the fluid loss additive or filter cake be substantially gone. To make fluid loss additives and filter cake components, acid-soluble or acid-reactive materials, such as but not limited to magnesia, aluminum hydroxide, calcite,

5   calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and sodium calcium magnesium polyphosphate glass are mixed with or incorporated into, solid acid-precursors, such as cyclic ester dimers of lactic acid or glycolic acid or homopolymers or copolymers of lactic acid or glycolic acid. These fluid loss additives and filter cake components are added to fluids injected into the subsurface in .

10   oilfield operations. At least a portion of the solid acid-precursors slowly hydrolyzes at controllable rates to release acids at pre-selected locations and times. The acids then react with and dissolve at least a portion of the acid-reactive materials. The result is that at least a portion of both the solid acid-precursor and the acid-reactive solid material dissolve. We will term this "self-destruction" of the mixture. This feature of these materials is used to improve

15   many oilfield treatments. Preferably most or all of the solid material initially added is no longer present at the end of the treatments. It is not necessary either for all of the solid acid-precursor to hydrolyze or for all of the solid acid-reactive material to dissolve. It is necessary only that a sufficient amount of either no longer be a solid portion of the filter cake so that the filter cake no longer forms a deleterious barrier to fluid flow.

20   Mixtures of one or more solid acid-precursors and one or more solid acid-reactive materials may be purely physical mixtures of separate particles of the separate components. The mixtures may also be manufactured such that one or more solid acid-precursors and one or more solid acid-reactive materials is in each particle; this will be termed a "combined mixture". This may be done, by non-limiting examples, by coating the acid-reactive material

25   with the solid acid-precursor, or by heating a physical mixture until the solid acid-precursor melts, mixing thoroughly, cooling, and comminuting. For example, it is common practice in industry to co-extrude polymers with mineral filler materials, such as talc or carbonates, so that they have altered optical, thermal and/or mechanical properties. Such mixtures of polymers and solids are commonly referred to as "filled polymers". When the solid acid-

30   reactive material is completely enclosed within the solid acid-precursor, the solid acid-reactive material may be water-soluble, for example boric acid or borax. In any case it is preferable for the distribution of the components in the mixtures to be as uniform as possible.

The relative amounts of the components may be adjusted for the situation to control the solid acid-precursor hydrolysis rate and the rate and extent of dissolution of the solid acid-reactive material. The most important factors will be the temperature at which the treatment will be carried out, the composition of the aqueous fluid or fluids with which the mixture will come

5   into contact, and the time desired for dissolution of the mixture.

The solid acid-precursors or the mixtures of solid acid-precursors and solid acid-reactive materials may be manufactured in various solid shapes, including, but not limited to fibers, beads, films, ribbons and platelets. The solid acid-precursors or the mixtures of solid acid-precursors and solid acid-reactive materials may be coated to slow the hydrolysis

10   further. Suitable coatings include polycaprolate (a copolymer of glycolide and epsilon-caprolactone), and calcium stearate, both of which are hydrophobic. Polycaprolate itself slowly hydrolyzes. Generating a hydrophobic layer on the surface of the solid acid-precursors or the mixtures of solid acid-precursors and solid acid-reactive materials by any means delays the hydrolysis. Note that coating here may refer to encapsulation or simply to

15   changing the surface by chemical reaction or by forming or adding a thin film of another material. Another suitable method of delaying the hydrolysis of the solid acid-precursor, and the release of acid, is to suspend the solid acid-precursor, optionally with a hydrophobic coating, in an oil or in the oil phase of an emulsion. The hydrolysis and acid release do not occur until water contacts the solid acid-precursor.

20   An advantage of the composition and method embodiments of the Invention is that, for a given oilfield treatment, the appropriate solid acid-precursor and solid acid-reactive material may be selected readily from among many available materials. The rate of acid generation from a particular solid acid-precursor or a particular mixture of a solid acid-precursor and a solid acid-reactive material, having a particular chemical and physical make-

25   up, including a coating if present, at a particular temperature and in contact with a fluid or fluids of a particular composition (for example pH and the concentration and nature of other components, especially electrolytes), is readily determined by a simple experiment: exposing the acid-precursor to the fluid or fluids under treatment conditions and monitoring the release of acid. The rate of solid acid-reactive material dissolution is governed by similar factors

30   (such as by the choice of solid acid-reactive material, the ratio of materials, the particle size, calcining and coating of solid acid-reactive material) and may readily and easily be

determined by similar experiments. Naturally, a solid acid-precursor is selected that a) generates acid at the desired rate (after a suitable delay if needed) and b) is compatible with and does not interfere with the function of other components of the fluid. An acid-reactive material is selected that dissolves in the evolving fluid at a suitable rate and is compatible

5   with the function of other components of the fluid. This is done for all of the methods described below.

The mixture self-destructs *in situ*, that is, in the location where it is placed. That location may be part of a suspension in a treatment fluid in the wellbore, in the perforations, in a gravel pack, or in a fracture; or as a component of a filter cake on the walls of a wellbore

10   or of a fracture; or in the pores of the formation itself. The mixture may be used in carbonates and sandstones. If the formation is significantly acid soluble, the amount of mixture, or the amount of solid acid-precursor in the mixtures, may be adjusted to account for consumption of acid in reaction with the formation. In use, even though the particles are intended to become part of a filter cake, they may end up in other places, where they are

15   normally undesirable because they impede fluid flow, so in all locations self-destruction is desired.

The particle sizes of the individual components of the mixture may be the same or different. The particle sizes of the individual components of the mixture or of the combined mixture, as they relate to the use as a fluid loss additive and as filter cake former components,

20   depend primarily upon the pore size distribution of the rock onto which the filter cake is to be deposited and whether or not it is intended to eliminate or just to reduce fluid loss. Criteria for, and methods of, choosing the optimal particle sizes or particle size distributions for conventional fluid loss additives and filter cake components are well known. Other particle sizes may be chosen for embodiments of the current Invention; particle sizes or size

25   distributions may be selected as a compromise between those that are optimal for fluid loss control or filter cake formation and those that are optimal for self-destruction at the desired time and rate. The rate of self-destruction can readily be measured in the laboratory in a given fluid at a given temperature.

A particular advantage of these materials is that the solid acid-precursors and the

30   generated acids are non-toxic and are biodegradable. The solid acid-precursors are often used as self-dissolving sutures.

The mixtures of solid acid-precursors and solid acid-reactive materials are used as fluid loss additives, optionally in combination with other materials, as components of filter-cake forming compositions. Mixtures in the form of particulates, fibers, films, ribbons or other shapes are added to the drilling, completion, or stimulation fluid to prevent or minimize
5 leakoff during reservoir drilling, drill-in, or stimulation operations – but in the long term they dissolve and eventually clean up without an additional treatment step. Furthermore, if the mixture is formulated so that it generates acid in excess of that required to dissolve the acid-reactive component, then the excess acid produced by hydrolysis stimulates the formation, if it contains acid-soluble material, by etching either the surface of naturally occurring fractures
10 or the face of the formation at the wellbore. Such mixtures that generate extra acid are particularly useful for drilling, "drill-in", and stimulation operations carbonate reservoirs, especially in fractured carbonate reservoirs. Also, an appropriate amount of buffer may be added to the fluid or to the particles to counteract the effects of acid being generated by premature hydrolysis of the solid acid-precursor.

15   Similarly, a self-destructing fluid leak-off and filter cake forming additive is made for drilling, completions, wellbore intervention and fracturing operations. A self-destructing drill-in fluid includes a mixture of the solid acid-precursor and an acid-soluble particulate material, such as but not limited to $CaCO_3$, aluminum hydroxide, or magnesia. This fluid creates a chemically metastable filtercake that prevents fluid leakoff and formation damage
20 during the drilling process but readily cleans up over time. As the solid acid-precursor hydrolyzes it forms an acid that attacks the carbonate or other particles and, since the solid acid-precursor and carbonates or other materials are intermingled during deposition, the cleanup process is uniform and extensive. In particularly preferred embodiments, the acid-soluble material has a high solubility in the *in situ* generated acid, that is, a given amount of
25 the acid dissolves a large amount of the acid-soluble material.

In hydraulic fracturing, frac-packing, and gravel packing embodiments, the solid acid-precursor may be added in the pad, throughout the treatment or to only some of the proppant or gravel stages. The solid acid-precursor or mixture may be a fiber in any of these uses and will retard flowback of proppant or gravel, and/or of fines if they are present, until the solid-
30 acid-precursor hydrolyzes and the mixture dissolves. A self-destructing fluid loss additive and filter cake is particularly useful in hydraulic fracturing, frac-packing, and gravel packing

because mechanical removal methods are impossible and methods involving contacting the fluid loss additive and filter cake with an additional fluid are not practical. For example, calcite is known to be an excellent fluid loss additive, but calcite is not soluble in water, even at 150 °C. Calcite has been used for years in drilling fluids to form filter cakes that are

5   subsequently removed with acid. Furthermore, solid acid-precursors such as polyglycolic acid soften and deform at high temperatures, whereas particles of materials such as magnesium oxide are hard. The deformation of the softened polyglycolic acid traps the magnesium oxide and makes it an even better fluid loss additive and filter cake former.

There are a number of composition embodiments of the Invention. In the simplest

10   embodiment, sized particles, beads, fibers, platelets or ribbons (or other shapes) of solid acid-precursor are mixed with sized particles of calcium carbonate in a drill-in fluid. It is also within the scope of the Invention to manufacture particles that contain both the solid acid-precursor and the acid-soluble particulate material, for example to co-extrude (and optionally then to comminute) mixtures of calcium carbonate and solid acid-precursor in particles,

15   fibers, platelets or ribbons that are used for this function. Calcium carbonate or other solid acid-reactive material coated with solid acid-precursor may also be used. In these uses, the tightness of the packing of the particles in the filtercake may also be used to control the rates of generation of acid and dissolution of particles by affecting local concentrations of reactants and products, convection, and other factors.

20   Another advantage to the use the mixtures of the Invention in fluid loss additives and filter cakes is that the acid generated in the self-destruction process may function as a breaker for polymeric or viscoelastic surfactant viscosifying agents. Acids are known to damage or destroy synthetic polymers and biopolymers used to viscosify drilling, completion and stimulation fluids. Acids are also known to damage or destroy either the micelle/vesicle

25   structures formed by viscoelastic surfactants or, in some cases, the surfactants themselves.

When solid acid-precursors or mixtures of solid acid-precursors and solid acid-reactive materials are used in fluids in such treatments as drilling, drill-in, completion, stimulation (for example, hydraulic fracturing or matrix dissolution), sand control (for example gravel packing, frac-packing, and consolidation), diversion, and others, the solid

30   acid-precursor or mixture of solid acid-precursor and solid acid-reactive material are initially inert to the other components of the fluids, so the other fluids may be prepared and used in

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the usual way. Normally, such fluids already contain a fluid loss additive and filter cake former, so the solid acid-precursor or mixture of solid acid-precursor and solid acid-reactive material replace some or all of the fluid loss additive and filter cake former that would otherwise have been used. In many cases, if the fluid contains a component that would affect

5   or be affected by the solid acid-precursor or mixture of solid acid-precursor and solid acid-reactive material (such as a buffer, another acid-reactive material, or a viscosifier that forms or is incorporated in filter cakes), either the amount or nature of the solid acid-precursor or mixture of solid acid-precursor and solid acid-reactive material or the amount or nature of the interfering or interfered-with component may be adjusted to compensate for the interaction.

10   This may readily be determined by simple laboratory experiments.

       Although the compositions and method embodiments of the Invention are described in terms of producing wells for oil and/or gas, the compositions and methods have other uses, for example they may also be used in injection wells (such as for enhanced recovery or for storage or disposal) or in production wells for other fluids such as carbon dioxide or water.

15   **Example 1.** Lactic acid is not as commonly used as an acid in oilfield treatments as are formic, acetic and citric acids. Tests were run to determine the capacity of lactic acid in the dissolution of calcite at 82 °C. Figure 1 shows the concentration of calcite in ppm dissolved by reagent grade lactic acid as a function of weight percent acid in water. Lactic acid has a capacity for dissolving calcite that is similar to acetic acid or formic acid, and

20   much higher than citric acid. These tests demonstrate that lactic acid generated from a lactate polymer is effective for dissolution of calcium carbonate.

       Example 2. Experiments were performed (Table 1) to evaluate the hydrolysis rate of PLA and to compare the hydrolysis rates of PLA with and without added calcite. The PLA was NATUREWORKS™ PLA Polylactide Resin 4042D, a polymerized mixture of D- and

25   L-lactic acid, available from Cargill Dow, Minnetonka, MN, USA. The material was used as approximately 4 mm diameter beads. The calcite was reagent grade powder. 45.04 Grams PLA and 20 grams calcite, when used, were added to 500 ml distilled water. The time shown is the time for 100 % hydrolysis.

Composition	121 °C	135 °C	149 °C

PLA	Dissolves in greater than 2 hours	Dissolves in greater than 2 hours	Dissolves in less than 2 hours
PLA + Calcite	Dissolves in greater than 2 hours 30 minutes	Dissolves in less than 2 hours 30 minutes	Dissolves in less than 45 minutes
Calcite	Insoluble	Insoluble	Insoluble

Table 1

These results show that this solid acid-precursor hydrolyses and dissolves at a rate suitable for use as a self-destructive fluid loss additive and filter cake former. Furthermore, calcite, which is insoluble in water under these conditions, accelerates the rate of PLA hydrolysis and is itself dissolved in the generated acid.

Example 3. Experiments were run to determine the suitability of various materials as fluid loss additives. Experimental conditions and results are shown in Table 2. Berea sandstone cores (2.54 cm long and 2.54 cm in diameter) were mounted in an API static fluid loss cell. Cores were flushed with 2% KCl brine, heated to the indicated temperature, and the permeability to the brine was determined at a flow rate of 5 ml/min. Then the indicated fluid was injected at a constant pressure of 6.895 MPa. The weight of effluent fluid was determined with a balance and recorded as a function of time. Leak-off was characterized in two ways: the "spurt", which was the initial rapid leak-off of fluid before a filter cake barrier was formed on the core face (indicated by the grams fluid leaked off in the first 30 seconds), and, "wall", which was the subsequent leak-off that occurred even after a filter cake was formed (indicated by the grams per minute of fluid leaked off between 15 and 30 minutes).

All concentrations shown in Table 2 are in weight percent. The surfactant used in all experiments was obtained from the supplier (Rhodia, Inc. Cranbury, New Jersey, U. S. A.) as Mirataine BET-E-40; it contains 40% active ingredient (erucylamidopropyl betaine), with the remainder being substantially water, sodium chloride, and isopropanol. The MgO used was MagChem 35, obtained from Martin Marietta Magnesia Specialties LLC, Baltimore, MD, USA. It has a mean particle size of 3 – 8 microns. The PGA used was Dupont TLF 6267, described by the supplier as a crystalline material having a molecular weight of about 600

and a mean particle size of about 8 to 15 microns. The Al(OH)$_3$ used was obtained from Aldrich. It has a mean particle size of about 40 microns. The PGA and the solid acid-reactive materials were added as separate particles. The buffer used in Experiment 25 was sodium sesquicarbonate.

5   These data show that all the mixtures of PGA and magnesium oxide, sized calcium carbonate, or aluminum hydroxide are excellent fluid loss additives and form filter cakes that very effectively reduce flow through these cores. (Without the additives, the flow through a 100 mD core would be greater than 100 g in a 30 minute test.) The fluid loss additives and filter cake formers are effective at various total concentrations and ratios of solid acid-10   precursor to solid acid-reactive material, in cores having a broad range of quite high permeabilities, and at several temperatures. They reduce both the spurt and the subsequent leak-off. Furthermore, when the composition of the Invention is used, a lower concentration of surfactant may be required.

Test ID	Run	Formulation	Temp.	Perm	g/30 min	Result "Spurt" g	"Wall" g/min
7598-11	1	3% Surfactant + 0.5% PGA + 0.4 % MgO	65.6C	167mD	17		
7598-113	2	3% Surfactant + 0.5% PGA + 0.4% MgO	65.6	137	23		
7598-114	3	3% Surfactant + 0.5% PGA + 0.4% MgO	65.6	152	11	2	0.29
7598-115	4	3% Surfactant + 0.5% PGA + 0.4% MgO	65.6	106	13		
7598-17	5	6% Surfactant + 0.5% PGA + 0.4% MgO	65.6	235	12		
7598-171	6	3% Surfactant + 0.5% PGA + 0.4% MgO	65.6	230	22		
7598-172	7	3% Surfactant + 0.5% PGA + 0.4% MgO	65.6	210	34		
7598-18	8	6% Surfactant + 0.5% PGA + 0.4% MgO	65.6	209	11		
7598-19	9	6% Surfactant + 0.5% PGA + 0.4% MgO	65.6	211	31		
7598-21	10	6% Surfactant + 0.5% MgO	65.6	125	23	7.5	0.37
7598-231	11	6% Surfactant + 0.2% PGA + 0.4% MgO	65.6	42	5.5		
7598-232	12	6% Surfactant + 0.2% PGA + 0.4% MgO	65.6	171	6	2	0.088
7598-233	13	6% Surfactant + 0.2% PGA + 0.4% MgO	65.6	306	7		
7598-24	14	3% Surfactant + 0.2% PGA + 0.4% MgO	65.6	246	19		
7598-25	15	6% Surfactant + 0.2% PGA + 0.4% MgO	93.3	29	7		
7598-251	16	6% Surfactant + 0.2% PGA + 0.4% MgO	93.3	126	7.5		
7598-252	17	6% Surfactant + 0.2% PGA + 0.4% MgO	93.3	299	9.5		
7598-28	18	3% Surfactant + 0.2% PGA + 0.4% MgO	93.3	51	17		
7598-281	19	3% Surfactant + 0.2% PGA + 0.4% MgO	93.3	119	18		
7598-29	20	3% Surfactant + 0.2% PGA + 0.4% MgO	93.3	300	20		
7598-31A	21	3% Surfactant + 0.2% PGA + 0.4% CaCO3 (2 micron)	65.6	48	29	7.5	0.52
7598-31B	22	3% Surfactant + 0.2% PGA + 0.4% CaCO3 (10 micron)	65.6	40	26		
7598-31C	23	6% Surfactant + 0.2% PGA + 0.4% CaCO3 (10 micron)	65.6	43	11	2.5	0.21
7598-31D	24	3% Surfactant + 0.2% PGA + 0.4% CaCO3 (2 micron) + 0.15% MgO	65.6	107	31		
7598-39B	25	3% Surfactant + 0.2% PGA + 0.4% Al(OH)3 + 0.2% Buffer	65.6	117	34	6	0.64
7598-39C	26	3% Surfactant + 0.2% PGA + 0.4% Al(OH)3	65.6	128	74	8	1.25

Table 2

What is claimed is:

1. An oilfield treatment composition comprising a mixture of a solid acid-precursor and a solid acid-reactive material.

5   2. The composition of claim 1 wherein the mixture is a physical mixture of particles.

3. The composition of claim 1 wherein the solid acid-precursor and the solid acid-reactive material are present in the same particle.

4. The composition of claim 3 wherein the solid acid-precursor surrounds the solid acid-reactive material.

10   5. The composition of claim 4 wherein the solid acid-reactive material is soluble in water.

6. The composition of claim 5 wherein the solid acid-reactive material is boric acid or borax.

7. The composition of any of claims 1 through 7 wherein the solid acid-precursor is
15   selected from the group consisting of lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and
20   mixtures thereof.

8. The composition of any of claims 1 through 4 and 7 wherein the solid acid-reactive material is selected from the group consisting of magnesium hydroxide, calcium carbonate, aluminum hydroxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and
25   sodium calcium magnesium polyphosphate glass.

9. The composition of any of the preceding claims wherein the solid acid-precursor is coated with a hydrolysis-delaying material.

10. An oilfield treatment method in which a filter cake is formed and at least partially destroyed on a subterranean formation surface comprising:

    a) preparing an oilfield treatment fluid comprising:

        i)   a solid acid-precursor, and

5   ii) a solid acid-reactive material;

    b) injecting said oilfield treatment fluid into a wellbore penetrating said formation, causing said fluid to contact said formation surface;

    c) forming a filter cake on said formation surface; and

    d) allowing at least a portion of said solid acid-precursor to hydrolyze,

10   whereby at least a portion of said solid acid-reactive material dissolves.

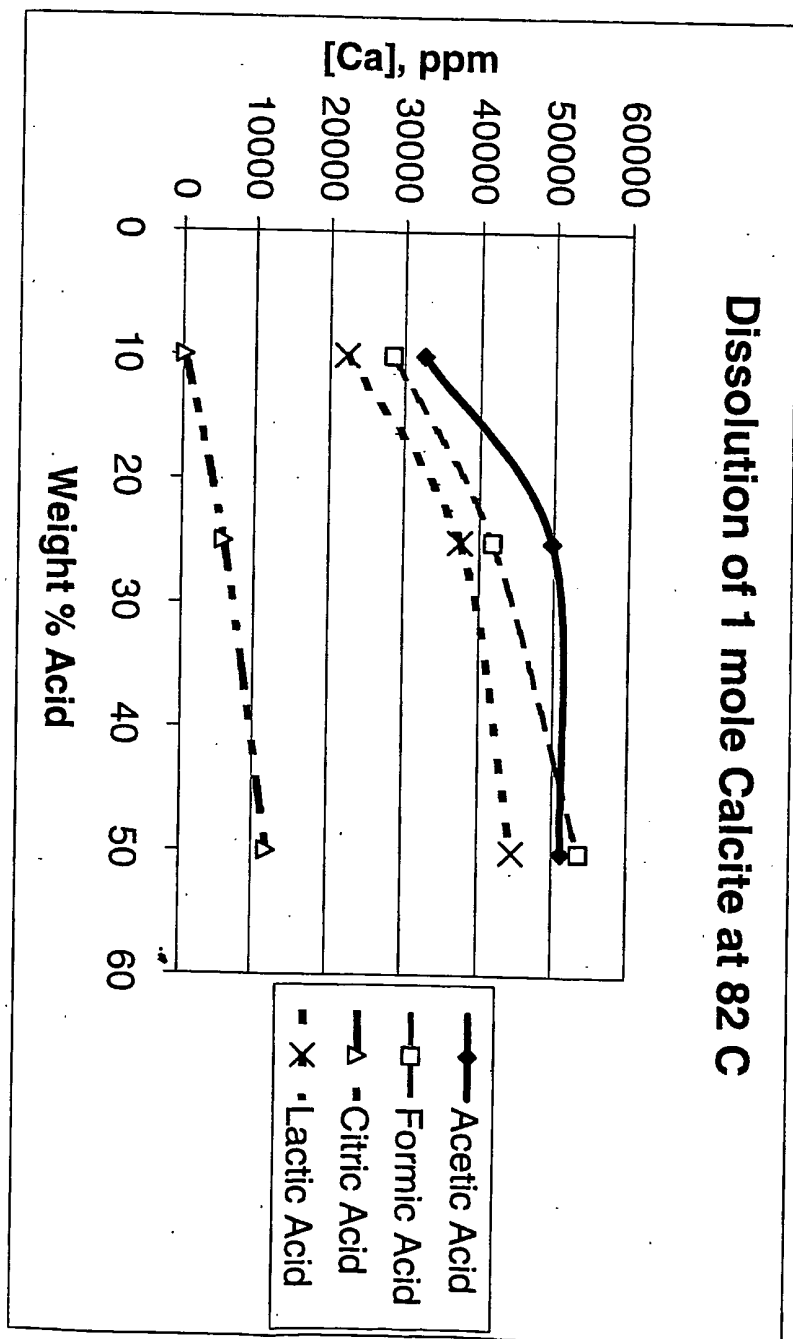FIG. 1

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C09K7/00   E21B33/138   E21B37/06   C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C09K   E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/142919 A1 (CONSTIEN VERNON GEORGE) 3 October 2002 (2002-10-03)	1,7
Y	paragraph '0011! – paragraph '0015! paragraph '0048! – paragraph '0050! claims 1,2,4,7,15-17	1,7,8,10
Y	EP 0 404 489 A (DU PONT ; CONOCO INC (US)) 27 December 1990 (1990-12-27) column 1, line 33 – line 42 column 2, line 36 – column 3, line 27; claims 1-3; example I	1,7,8,10
A	WO 00/78890 A (SOFITECH NV ; SCHLUMBERGER CA LTD (CA); BRAND FABIEN J (FR); DOWELL SC) 28 December 2000 (2000-12-28) page 4, line 1 – line 11	1-5,8

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 January 2004	02/02/2004

| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Authorized officer Boulon, A |

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 131 661 A (CONNER RICHARD PAUL ET AL) 17 October 2000 (2000-10-17) column 3, line 37 - column 4, line 12	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

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(54) Title: GENERATING ACID DOWNHOLE IN ACID FRACTURING

Dissolution of 1 mole Calcite at 82 C
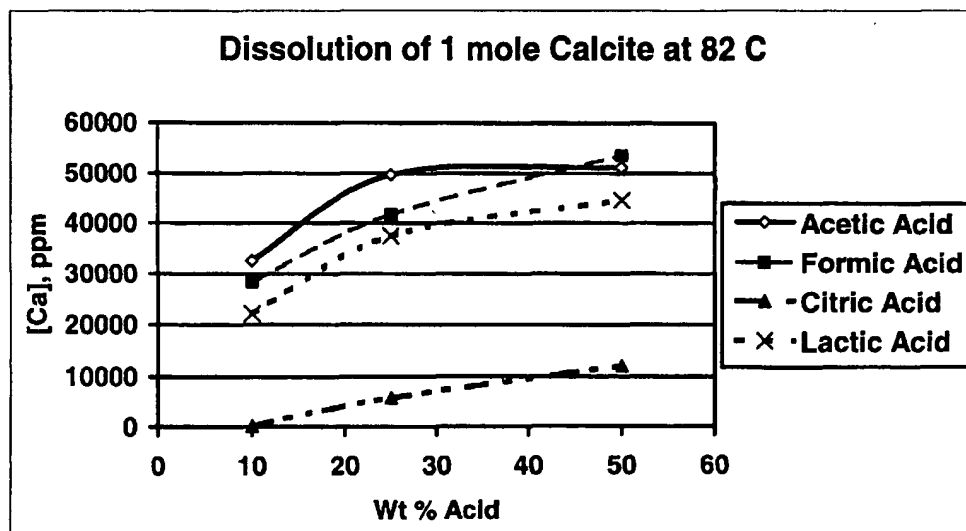
(57) Abstract: An acid fracturing method is provided in which the acid is generated in the fracture by hydrolysis of a solid acid-precursor selected from one or more than one of lactide, glycolide, polylactic acid, polyglycolic acid, a copolymer of polylactic acid and polyglycolic acid, a copolymer of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and a copolymer of lactic acid with other hydroxy-, carboxylic acid or hydroxycarboxylic acid-containing moieties. The solid acid-precursor may be mixed with a solid acid-reactive material to accelerate the hydrolysis and/or coated to slow the hydrolysis. Water-soluble liquid compounds are also given that accelerate the hydrolysis. The method ensures that the acid contacts fracture faces far from the wellbore.

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

GENERATING ACID DOWNHOLE IN ACID FRACTURING

Background of the Invention

This invention relates to a method of injecting solid acid-precursors that dissolve

5   in water to generate acids after they have been injected. More particularly it relates to a method of generating acids *in situ* far from the wellbore in fractures in acid fracturing (fracture acidizing).

In acid fracturing, acid is placed in the fracture, at a distance from the wellbore, where it reacts with the face of the fracture to etch differential flow paths that a) create

10   disparities so that the opposing fracture faces do not match up when the fracture pressure is released and so the fracture does not close completely, and b) provide flow paths for produced fluid along the fracture faces from distant portions of the fracture toward the wellbore. Normally, the acid is placed in the desired location by forming an acidic fluid on the surface and pumping the acidic fluid from the surface and down the wellbore

15   above fracture pressure. There are generally two major problems encountered during this normal procedure.

First, in the pumping operation the acid is in contact with iron-containing components of the wellbore such as casing, liner, coiled tubing, etc. Acids are corrosive to such materials, especially at high temperature. This means that corrosion inhibitors

20   must be added to the fluid being injected in order not to limit the amount of acid, and/or the time of exposure, that can be used during injection of an acid. Furthermore, acid corrosion creates iron compounds such as iron chlorides. These iron compounds may precipitate, especially if sulfur or sulfides are present, and may interfere with the stability or effectiveness of other components of the fluid, thus requiring addition of iron control

25   agents or iron sequestering agents to the fluid.

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Second, if, as is usually the case, the intention is to use the acid to treat a part of the formation at a significant distance away from the wellbore, this may be very difficult to accomplish because if an acid is injected from the surface down a wellbore and into contact with the formation, the acid will naturally react with the first reactive material

5   with which it comes into contact. Depending upon the nature of the well and the nature of the treatment, this first-contacted and/or first-reacted material may be a filtercake, may be the formation surface forming the wall of an uncased (or openhole) wellbore, may be the near-wellbore formation, or may be a portion of the formation that has the highest permeability to the fluid, or is in fluid contact with a portion of the formation that has the

10   highest permeability to the fluid. In many cases, this may not be the formation (matrix) material with which the operator wants the acid to react. At best this may be wasteful of acid; at worst this may make the treatment ineffective or even harmful. In general, the higher the temperature the more reactive is the acid and the greater are the problems.

There are several ways in which operators have dealt with these problems in the

15   past. One method is to segregate the acid from the material with which reaction is not desired. This is done, for example, by a) placing the acid in the internal phase of an emulsion (so-called "emulsified acid") and then either causing or allowing the emulsion to invert at the time and place where reaction is desired or allowing slow transport of the acid across the phase boundaries, or b) encapsulating the acid, for example by the method

20   described in U.S. Patent No. 6,207,620, and then releasing the acid when and where it is needed. There are problems with these methods. Although emulsified acids are popular and effective, they require additional additives and specialized equipment and expertise, and may be difficult to control. A problem with the encapsulated acids is that the location and timing of release of the acid may be difficult to control. The release is

25   brought about by either physical or chemical degradation of the coating. Physical damage to the encapsulating material, or incomplete or inadequate coating during manufacture, could cause premature release of the acid.

A second method is to delay formation of the acid. Templeton, et al., in "Higher pH Acid Stimulation Systems", SPE paper 7892, 1979, described the hydrolysis of esters

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such as methyl formate and methyl acetate as *in situ* acid generators in the oilfield. 1ney also described the reaction of ammonium monochloroacetic acid with water to generate glycolic acid and ammonium chloride in the oilfield. However, these acid precursors are liquids, and these reactions take place very rapidly as soon as the acid precursors contact

5   water.

There is a need for a new method of delayed, controlled release of acids from solids *in situ* in acid fracturing.

Summary of the Invention

One embodiment of the Invention is a method of acid fracturing using a solid

10   acid-precursor for providing a controlled release of acid by hydrolysis and dissolution. The solid acid-precursor is lactide, glycolide, polylactic acid, polyglycolic acid, a copolymer of polylactic acid and polyglycolic acid, a copolymer of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, a copolymer of lactic acid with other hydroxy-, carboxylic acid or hydroxycarboxylic acid-

15   containing moieties, or mixtures of the preceding. The solid acid-precursor may be mixed with a second solid that reacts with an acid, such as magnesium hydroxide, magnesium carbonate, dolomite (magnesium calcium carbonate), calcium carbonate, aluminum hydroxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and sodium calcium magnesium

20   polyphosphate glass for the purpose of increasing the rate of dissolution and hydrolysis of the solid acid-precursor. The second solid will be called a "solid acid-reactive material". In embodiments of the Invention, the particles of solid acid-precursors, optionally mixed with solid acid-reactive materials in the same or separate particles, are in the form of beads, ribbons, platelets, fibers or other shapes. When they are in the same particles, the

25   solid acid-precursors may enclose the solid acid-reactive materials. The solid acid-precursor, including when it is mixed with or contains other materials, may itself be coated or encapsulated to slow or delay hydrolysis. In another embodiment, soluble liquids such as esters, diesters, anhydrides, lactones, sodium hydroxide, potassium

hydroxide, amides, amines, carbonates, bicarbonates, alcohols, alkanol amines, ammonium hydroxide and mixtures thereof are added to the fracture fluid to accelerate the hydrolysis of the solid acid-precursor. In another embodiment, the fluid further contains a proppant. In yet another embodiment the fluid further contains a viscosifier.

5   In a still further embodiment the fluid further contains a proppant and a viscosifier. In a further embodiment the fluid contains an acid, for example hydrochloric acid, hydrofluoric acid, ammonium bifluoride, formic acid, acetic acid, lactic acid, glycolic acid, an aminopolycarboxylic acid, a polyaminopolycarboxylic acid, a salt of one or more of these acids or a mixture of one or more of these acids or salts.

10   **Brief Description of the Drawings**

Figure 1 shows the solubility of calcite in various organic acids.

Detailed Description of the Invention

Unlike conventional acid fracturing, the fracturing fluid used in the method of the Invention does not normally contain an acid when it is prepared at the surface and

15   injected into the wellbore.

Excellent sources of acid that can be generated downhole when and where it is needed are solid cyclic dimers, or solid polymers, of certain organic acids, that hydrolyze under known and controllable conditions of temperature, time and pH to form the organic acids. We will call these solid materials "acid-precursors" and we will call the formation

20   of acid downhole "delayed acid generation". One example of a suitable solid acid-precursor is the solid cyclic dimer of lactic acid (known as "lactide"), which has a melting point of 95 to 125 °C, (depending upon the optical activity). Another is a polymer of lactic acid, (sometimes called a polylactic acid (or "PLA"), or a polylactate, or a polylactide). Another example is the solid cyclic dimer of glycolic acid (known as

25   "glycolide"), which has a melting point of about 86 °C. Yet another example is a polymer of glycolic acid (hydroxyacetic acid), also known as polyglycolic acid ("PGA"),

or polyglycolide. Another example is a copolymer of lactic acid and glycolic acid. These polymers and copolymers are polyesters.

Cargill Dow, Minnetonka, MN, USA, produces the solid cyclic lactic acid dimer called "lactide" and from it produces lactic acid polymers, or polylactates, with varying

5   molecular weights and degrees of crystallinity, under the generic trade name NATUREWORKS™ PLA. The PLA's currently available from Cargill Dow have molecular weights of up to about 100,000, although any polylactide (made by any process by any manufacturer) and any molecular weight material of any degree of crystallinity may be used in the embodiments of the Invention. The PLA polymers are

10   solids at room temperature and are hydrolyzed by water to form lactic acid. Those available from Cargill Dow typically have crystalline melt temperatures of from about 120 to about 170 °C, but others are obtainable. Poly(d,l-lactide) is available from Bio-Invigor, Beijing and Taiwan, with molecular weights of up to 500,000. Bio-Invigor also supplies polyglycolic acid (also known as polyglycolide) and various copolymers of

15   lactic acid and glycolic acid, often called "polyglactin" or poly(lactide-co-glycolide). The rates of the hydrolysis reactions of all these materials are governed by the molecular weight, the crystallinity (the ratio of crystalline to amorphous material), the physical form (size and shape of the solid), and in the case of polylactide, the amounts of the two optical isomers. (The naturally occurring l-lactide forms partially crystalline polymers;

20   synthetic dl-lactide forms amorphous polymers.) Amorphous regions are more susceptible to hydrolysis than crystalline regions. Lower molecular weight, less crystallinity and greater surface-to-mass ratio all result in faster hydrolysis. Hydrolysis is accelerated by increasing the temperature, by adding acid or base, or by adding a material that reacts with the hydrolysis product(s).

25   Homopolymers can be more crystalline; copolymers tend to be amorphous unless they are block copolymers. The extent of the crystallinity can be controlled by the manufacturing method for homopolymers and by the manufacturing method and the ratio and distribution of lactide and glycolide for the copolymers. Polyglycolide can be made

in a porous form. Some of the polymers dissolve very slowly in water before they hydrolyze.

Other materials suitable as solid acid-precursors are all those polymers of hydroxyacetic acid (glycolic acid) with itself or other hydroxy-, carboxylic acid-, or 5 hydroxycarboxylic acid-containing moieties described in U.S. Patent Nos. 4, 848,467; 4,957,165; and 4,986,355.

It has been found that dissolution of the solid acid-precursors of the Invention is accelerated by the addition of certain chemical agents. These agents react readily with the solid acid-precursor and cause the removal of a small amount of material from the 10 solid acid-precursor surface. Not to be limited by theory, but it is believed that an intact surface of the solid acid-precursor is comparatively insoluble, but that when the surface is disrupted by the removal of a small amount of material subsequent dissolution of additional material from that surface is easier. Only a small amount of the accelerating agent ("accelerant") is necessary to start the dissolution process; thereafter it will proceed 15 without any added agent. On the other hand, if there is additional agent present, since it reacts readily with the solid acid-precursor it will accelerate the continuing dissolution process. This is the "accelerant" mechanism. Note that the accelerant does not consume all of the acid generated; it causes more rapid generation of more acid by disrupting the solid acid-precursor surface structure. If the agent is a solid, it cannot accelerate the 20 initial dissolution because there is inadequate chemical interaction between the two solids, but once the dissolution of the solid acid-precursor starts (for example as a result of an increase in temperature) the solid acid-reactive material will accelerate subsequent dissolution. Note that the formation itself can be a solid accelerant. Furthermore, the action of accelerants may be delayed, for example, if the are slowly soluble solids or if 25 they are chemically bound in a liquid chemical that must be hydrolyzed to release the agent. One solid acid-precursor may be an accelerant for another; for example, PGA accelerates the hydrolysis of PLA. The timing and rate of dissolution of the solid acid-precursor is controlled by these techniques.

To accelerate the dissolution of solid acid-precursors, water-insoluble solid acid-soluble or acid-reactive materials, such as but not limited to magnesium hydroxide, magnesium carbonate, dolomite (magnesium calcium carbonate), calcium carbonate, aluminum hydroxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, 5   sodium zinc potassium polyphosphate glass, and sodium calcium magnesium polyphosphate glass, may be mixed with or incorporated into, solid acid-precursors, such as cyclic ester dimers of lactic acid or glycolic acid or homopolymers or copolymers of lactic acid or glycolic acid. These mixtures are added to the fracturing fluid. At least a portion of the solid acid-precursor slowly hydrolyzes at controllable rates to release acids 10   at pre-selected locations and times in the fracture. In addition to reacting with the formation fracture face, the acids also react with and dissolve at least a portion of the acid-reactive materials, if they are present. This will accelerate the dissolution of the solid acid-precursor and generate acid in amounts beyond that which reacts with the solid acid-reactive material. The result is that at least a portion of both the solid acid-precursor 15   and the acid-reactive solid material dissolve. Usually most or all of the solid material initially added is no longer present at the end of the treatment. However, it is not necessary either for all of the solid acid-precursor to hydrolyze or for all of the solid acid-reactive material to dissolve. Any solids remaining will beneficially act as proppant. Note that often the additional solid acid-reactive material will not be needed to accelerate 20   the hydrolysis of the solid acid-precursor, because the formation itself will be acid-reactive. However, the solid acid-reactive material may be selected to be more reactive than the formation or may be in more intimate contact with the solid acid-precursor.

The dissolution of solid acid-precursors in acid fracturing may also be accelerated by the addition of certain soluble liquid additives. These accelerants may be acids, bases, 25   or sources of acids or bases. These are particularly valuable at low temperatures (for example below about 135 °C), at which the solid acid-precursors hydrolyze slowly, relative to the time an operator would like to put a well on production after a fracturing treatment. Non-limiting examples of such soluble liquid additives that hydrolyze to release organic acids are esters (including cyclic esters), diesters, anhydrides, lactones 30   and amides. A compound of this type, and the proper amount, that hydrolyzes at the

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appropriate rate for the temperature of the formation and the pH of the fracturing fluid is readily identified for a given treatment by simple laboratory hydrolysis experiments. Other suitable soluble liquid additives are simple bases. (They are termed "liquids" because in practice it would be simpler and safer to add them to the fracturing fluid as

5 aqueous solutions rather than as solids.) Suitable bases are sodium hydroxide, potassium hydroxide, and ammonium hydroxide. Other suitable soluble liquid additives are alkoxides, water-soluble carbonates and bicarbonates, alcohols such as but not limited to methanol and ethanol, alkanol amines and organic amines such monoethanol amine and methyl amine. Other suitable soluble liquid additives are acids, such as but not limited to

10 hydrochloric acid, hydrofluoric acid, ammonium bifluoride, formic acid, acetic acid, lactic acid, glycolic acid, aminopolycarboxylic acids (such as but not limited to hydroxyethyliminodiacetic acid), polyaminopolycarboxylic acids (such as but not limited to hydroxyethylethylenediaminetriacetic acid), salts -- including partial salts -- of the organic acids (for example, ammonium, potassium or sodium salts), and mixtures of

15 these acids or salts. (Ammonium bifluoride partially hydrolyzes in contact with water to form some HF, and so will be called an acid here.) The organic acids may be used as their salts. When corrosive acid might contact corrodible metal, corrosion inhibitors are added.

Mixtures of one or more solid acid-precursors and one or more solid acid-reactive

20 materials, if they are present, may be purely physical mixtures of separate particles of the separate components. The mixtures may also be manufactured such that one or more solid acid-precursors and one or more solid acid-reactive materials is in each particle; this will be termed a "combined mixture". This may be done, by non-limiting examples, by coating the acid-reactive material with the solid acid-precursor, or by heating a physical

25 mixture until the solid acid-precursor melts, mixing thoroughly, cooling, and comminuting. For example, it is common practice in industry to co-extrude polymers with mineral filler materials, such as talc or carbonates, so that they have altered optical, thermal and/or mechanical properties. Such mixtures of polymers and solids are commonly referred to as "filled polymers". In any case it is preferable for the

30 distribution of the components in the mixtures to be as uniform as possible. The choices

and relative amounts of the components may be adjusted for the situation to control tne

solid acid-precursor hydrolysis rate. The most important factors will be the temperature

at which the treatment will be carried out, the composition of the aqueous fluid or fluids

with which the mixture will come into contact, and the time and rate desired for

5   generation of the acid.

The solid acid-precursors or the mixtures of solid acid-precursors and solid acid-

reactive materials may be manufactured in various solid shapes, including, but not limited

to fibers, beads, films, ribbons and platelets. The solid acid-precursors or the mixtures of

solid acid-precursors and solid acid-reactive materials may be coated to slow the

10   hydrolysis. Suitable coatings include polycaprolate (a copolymer of glycolide and

epsilon-caprolactone), and calcium stearate, both of which are hydrophobic.

Polycaprolate itself slowly hydrolyzes. Generating a hydrophobic layer on the surface of

the solid acid-precursors or the mixtures of solid acid-precursors and solid acid-reactive

materials by any means delays the hydrolysis. Note that coating here may refer to

15   encapsulation or simply to changing the surface by chemical reaction or by forming or

adding a thin film of another material. Another suitable method of delaying the

hydrolysis of the solid acid-precursor, and the release of acid, is to suspend the solid acid-

precursor, optionally with a hydrophobic coating, in an oil or in the oil phase of an

emulsion. The hydrolysis and acid release do not occur until water contacts the solid

20   acid-precursor. Methods used to delay acid generation may be used in conjunction with

inclusion of solid acid-reactive material to accelerate acid generation because it may be

desirable to delay acid generation but then to have acid generated rapidly.

An advantage of the composition and method embodiments of the Invention is

that, for a given oilfield treatment, the appropriate solid acid-precursor and solid acid-

25   reactive material may be selected readily from among many available materials. The rate

of acid generation from a particular solid acid-precursor or a particular mixture of a solid

acid-precursor and a solid acid-reactive material, having a particular chemical and

physical make-up, including a coating if present, at a particular temperature and in

contact with a fluid or fluids of a particular composition (for example pH and the

concentration and nature of other components, especially electrolytes), is readily
determined by a simple experiment: exposing the acid-precursor to the fluid or fluids
under treatment conditions and monitoring the release of acid. The rate of solid acid-
reactive material dissolution, if the solid acid-reactive material is included, is governed
by similar factors (such as by the choice of solid acid-reactive material, the ratio of
materials, the particle size, calcining and coating of solid acid-reactive material) and may
readily and easily be determined by similar experiments. Naturally, a solid acid-
precursor is selected that a) generates acid at the desired rate (after a suitable delay if
needed) and b) is compatible with and does not interfere with the function of other
components of the fluid. An acid-reactive material is selected that accelerates acid
generation to a suitable extent and is compatible with the function of other components of
the fluid.

The solid acid-precursor particles, or the mixture particles, self-destruct *in situ*,
that is, in the location where they are placed (deliberately or inadvertently). That location
may be part of a suspension in a treatment fluid in the wellbore, in the perforations, in a
fracture, as a component of a filter cake on the walls of a wellbore or of a fracture, or in
the pores of the formation itself. The method may be used in carbonates and sandstones.
In use, even though the particles are intended to be in a fracture, they may end up in other
places, where they are normally undesirable because they impede fluid flow, so in all
locations self-destruction is desired. The great majority of the particles end up in a
fracture where the acid that is generated etches the fracture faces.

If a mixture is used, the particle sizes of the individual components of the mixture
may be the same or different. Almost any particle size may be used. Governing factors
include a) the capability of equipment, b) the width of the fracture generated, and c) the
desired rate and time of self-destruction. The rate of self-destruction can readily be
measured in the laboratory in a given fluid at a given temperature. Preferred sizes are
those of proppants and fluid loss additives since operators have the equipment and
experience suitable for those sizes.

A particular advantage of these materials is that the solid acid-precursors and tne generated acids are non-toxic and are biodegradable. The solid acid-precursors are often used as self-dissolving sutures.

5   The solid acid-precursors of the current Invention may be used for delayed acid generation in acid fracturing in the ways in which the encapsulated acids described in U.S. Patent No. 6,207,620, hereby incorporated in its entirety, are used.

The solid acid-precursors, with or without accelerants, may be used particularly effectively in acid fracturing treatments. Acid fracturing is a process in which an acidic fluid is injected into a formation at a pressure sufficiently high to fracture the rock; the
10   acid then etches the surfaces of the fracture so that conductive flow paths are formed, along the fracture faces, that remain after the pressure is released and the fracture faces are forced back together. There are potentially serious problems encountered with acid fracturing. First, acids, especially strong acids, react with the first material they encounter. In an acid fracturing treatment, as in matrix acidizing treatments, this means
15   that as soon as a fracture forms or is enlarged, or as soon as a high permeability region is formed or encountered, both of which are likely to occur near the wellbore, acid will contact the fresh matrix surface near the wellbore, or in fluid contact with the high permeability region near the wellbore, and react with it. Most or all of the acid reaction then occurs near the wellbore, or in or near the high permeability region near the
20   wellbore, and little or none of the acid reaches portions of the fracture farther from the wellbore, or farther away than the high permeability region. Therefore etched flow paths along the fracture faces are not formed very far away from the wellbore or beyond any high permeability regions. Second, once the acid begins to react with a portion of the matrix material, it tends to form "wormholes" or paths of least resistance that subsequent
25   acid will follow. If either or both of these occurs, then when the pressure is released and the fracture closes, a satisfactory flow path for production of fluids, from the formation into the fracture and then into the wellbore, will not be formed. Solid acid-precursors solve these problems. Because the fluid is not sufficiently acidic when it is first injected, it will not react with the first formation material with which it comes into contact; rather

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it will be carried farther into the growing fracture where the acid will subsequently react when it is released. Also, because the acid-precursor is a solid material, if it is large it will help prop open the fracture until the differential etching occurs, but then after it is hydrolyzed the solid acid-precursor will no longer be present and so if it is small it will

5   not impede fluid flow from the formation into the wellbore for production.

Thus one embodiment of the Invention is a method of acid fracturing with a solid acid-precursor present in the fracturing fluid. This may be done in several ways. The solid acid-precursor is sometimes included in an otherwise conventional acid fracturing treatment (in which the fluid contains an acid such as HCl, HF, an organic acid or

10   mixtures thereof). The initially present acids will tend to spend in the near-wellbore or high permeability region of the formation, but the solid acid-precursor will be carried farther into the fracture and generate acid *in situ* that will etch the fracture faces farther from the wellbore. Most commonly, the solid acid-precursor is the only source of acid in the treatment. Optionally, in an acid fracturing treatment in which the acid is generated

15   from a solid acid-precursor, proppant may be included to help keep the fracture open until the solid acid-precursor has hydrolyzed and dissolved.

In acid fracturing, large amounts of solid acid-precursor are typically desirable. Rapid dissolution of the solid acid-precursor is typically desirable (as long as too much dissolution does not occur too close to the wellbore) because if the particles dissolve too

20   slowly then even dissolution of the formation rather than differential etching of fracture faces may result. Corrosion inhibitor should be added in case particles are trapped, before they reach the fracture, in a place where their dissolution will generate an acid that will contact metal components. An appropriate amount of buffer may be added to the fluid or to the particles to counteract the effects of acid being generated by premature

25   hydrolysis of the solid acid-precursor.

In an important embodiment, the solid acid-precursor (with or without any additional solid acid-reactive material) is used in a fracturing treatment in which it is the only source of acid; it also acts as a proppant until it hydrolyzes. (Normally proppant is

not used in acid fracturing, although it can be and such use would be within the scope of the Invention.) The solid acid-precursor is pumped into the well and at temperature, hydrolyses to the active acid, and reacts with the surface of the rock. Such treatments are conducted as cost-minimization water fracs in which a low concentration, for example

5   about 0.05 kg/L, of solid acid-precursor or mixture is pumped at a high rate, for example up to about 3500 L/min or more, with little or no viscosifier. They are also conducted, as are more conventional fracturing treatments, with viscosifiers and higher concentrations, for example up to about 0.6 kg/L, of solid acid-precursor or mixture. The viscosifiers are the polymers or viscoelastic surfactants typically used in fracturing, frac-packing and

10   gravel packing. In this case the solid acid-precursor or mixture acts as a proppant and is preferably in the form of beads in the size range typically used for proppants in hydraulic fracturing. When a large amount of particles of solid acid-precursor or mixture is used, this may necessitate using a more viscous fluid than is usually used in conventional acid fracturing. The lower density of the solid acid-precursor or mixture, relative to the

15   density of conventional proppants, is an advantage since the amount of viscosifier needed is less. The solid acid-precursor or mixture also acts as a breaker for the viscosifier, thus enhancing cleanup and offsetting any damage that might be done by the viscosifier. (Acids are known to damage or destroy synthetic polymers and biopolymers used to viscosify drilling, completion and stimulation fluids. Acids are also known to damage or

20   destroy either the micelle/vesicle structures formed by viscoelastic surfactants or, in some cases, the surfactants themselves.) In another embodiment, at least a portion of the solid acid-precursor or mixture is in the form of fibers. Fibers are known to assist in the transport of more spherical particles, reducing or eliminating the need for viscosification.

        The amount of solid acid-precursor or mixture used per unit area of fracture to be
25   created, depends upon, among other factors, the temperature and the amount of acid needed. The preferred concentration range is between about 0.42 and about 5 ppg (between about 0.05 and about 0.6 kg/L). The most preferred range is between about 0.83 and about 2.5 ppg (between about 0.1 and about 0.3 kg/L).

Although one of the principle benefits of the method of the Invention is that little or no diversion is required to divert acid from wormholes or high permeability regions being created during the treatment, diverters may still be used to divert the fluid containing a solid acid-reactive material from already-present high permeability streaks,

5   vugs, or natural fractures.

In addition to etching fracture faces to increase fracture conductivity, acid generated from solid acid-precursors serves a number of other useful functions, for example as a breaker or breaker aid for polymer or viscoelastic surfactant thickeners if they are present, as a dissolver of fluid loss additives, or as a dissolver of scales or fines,

10   etc.

There are a number of particle shapes that are used in the Invention. In the simplest embodiment, sized particles, beads, fibers, platelets or ribbons (or other shapes) of solid acid-precursor are used. It is also within the scope of the Invention to manufacture particles that contain both the solid acid-precursor and the acid-soluble

15   particulate material, for example to co-extrude mixtures of calcium carbonate and solid acid-precursor in particles, fibers, platelets or ribbons that are used for this function. Calcium carbonate (or other solid acid-reactive materials) coated with solid acid-precursor may also be used. The concentration of particles in the fracture or the tightness of the packing of the particles in the fracture may also be used to control the rates of

20   generation of acid and dissolution of particles by affecting local concentrations of reactants and products, convection, and other factors. It is also within the scope of the Invention to manufacture particles that contain both the solid acid-precursor and an acid-soluble particulate material, for example to co-extrude (and optionally then to comminute) mixtures of solid acid-reactive material and solid acid-precursor in particles,

25   fibers, platelets, ribbons or other shapes. Calcium carbonate or other solid acid-reactive material coated with solid acid-precursor may also be used.

When solid acid-precursors or mixtures of solid acid-precursors and solid acid-reactive materials are used in acid fracturing, with or without soluble accelerants, the

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solid acid-precursor or mixture of solid acid-precursor and solid acid-reactive material are initially inert to any other components of the fluids, so the other fluids may be prepared and used in the usual way. Any additives used in oilfield treatment fluids may also be included provided that they are compatible with, and do not interfere with the

5   performance of, the solid acid-precursor and/or the solid acid-reactive material and/or soluble liquid accelerants, if the are used, and vice versa. If the fluid contains a component (such as a buffer or a viscosifier) that would affect or be affected by the solid acid-precursor or mixture of solid acid-precursor and solid acid-reactive material or soluble liquid accelerant, then either the amount or nature of the solid acid-precursor or

10   mixture of solid acid-precursor and solid acid-reactive material or soluble liquid accelerant, or the amount or nature of the interfering or interfered-with component may be adjusted to compensate for the interaction. This may readily be determined by simple laboratory experiments.

Although the compositions and method embodiments of the Invention are

15   described in terms of producing wells for oil and/or gas, the compositions and methods have other uses, for example they may also be used in injection wells (such as for enhanced recovery or for storage or disposal) or in production wells for other fluids such as carbon dioxide or water.

Example 1. Lactic acid is not as commonly used as an acid in oilfield treatments

20   as are formic, acetic and citric acids. Tests were run to determine the capacity of lactic acid in the dissolution of calcite at 82 °C. Figure 1 shows the concentration of calcite in ppm (measured as Ca^{++} by ICP-AES) dissolved by reagent grade lactic acid as a function of weight percent acid in water. Lactic acid has a capacity for dissolving calcite that is similar to acetic acid or formic acid, and much higher than citric acid. These tests

25   demonstrate that lactic acid generated from a lactate polymer is effective for dissolution of calcium carbonate.

Example 2. Experiments were performed (Table 1) to evaluate the hydrolysis rate of PLA and to compare the hydrolysis rates of PLA with and without added calcite. The

PLA was NATUREWORKS™ PLA Polylactide Resin 4042D, a polymerized mixture of
D- and L-lactic acid, available from Cargill Dow, Minnetonka, MN, USA. The material
was used as approximately 4 mm diameter beads. The calcite was reagent grade powder.
45.04 Grams PLA and 20 grams calcite, when used, were added to 500 ml distilled water.
5　　The time shown is the time for 100 % hydrolysis.

Composition	121 °C	135 °C	149 °C
PLA	Dissolves in greater than 2 hours	Dissolves in greater than 2 hours	Dissolves in less than 2 hours
PLA + Calcite	Dissolves in greater than 2 hours 30 minutes	Dissolves in less than 2 hours 30 minutes	Dissolves in less than 45 minutes
Calcite	Insoluble	Insoluble	Insoluble

Table 1

In another experiment, a sample of a biaxially stretched PLA film (about 0.02 mm
thick and cut into pieces about 25 mm by about 25 mm) obtained as
NATUREWORKS™ BOPLA Biaxially Oriented Poly Lactic Acid Film MLF 100 from
10　　Cargill Dow, Minnetonka, MN, USA, was found to be approximately as readily dissolved
in distilled water at 149 °C as was the NATUREWORKS™ PLA Polylactide Resin
4042D. These results show that these solid acid-precursors hydrolyze and dissolve at a
rate suitable for use as an acid source in acid fracturing and that they dissolve calcite.
Furthermore, calcite, which is insoluble in water under these conditions, accelerates the
15　　rate of PLA hydrolysis.

Example 3. Experiments were conducted to demonstrate the efficacy of soluble
liquid accelerants. 45.04 Grams NATUREWORKS™ PLA Polylactide Resin 4042D
was added to 500 ml distilled water. This would be 1 molar lactic acid if fully
hydrolyzed. Varying amounts of accelerant, giving concentrations ranging from about

0.1 molar to about 1 molar were added. The mixture was then stirred at 90 °C. After X hours, complete hydrolysis was not observed. Sodium hydroxide was found to be approximately as reactive as propylene glycol diacetate; those two were more reactive than potassium hydroxide, which was more reactive than ammonium hydroxide. Once the PLA dissolution was initiated, the rate was not affected by the concentration of added component.

What is claimed is:

1. A method of acid fracturing a subterranean formation penetrated by a wellbore comprising:

   a) injecting a fluid comprising a solid acid-precursor, and

5   b) allowing at least a portion of the solid acid-precursor to hydrolyze.

2. The method of claim 1 wherein the solid acid-precursor is selected from the group consisting of lactide, glycolide, polylactic acid, polyglycolic acid, copolymers of polylactic acid and polyglycolic acid, copolymers of glycolic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties,

10   copolymers of lactic acid with other hydroxy-, carboxylic acid-, or hydroxycarboxylic acid-containing moieties, and mixtures thereof.

3. The method of claim 1 or claim 2 wherein the solid acid-precursor is mixed with a solid acid-reactive material.

4. The method of claim 3 wherein the solid acid-reactive material is selected from

15   the group consisting of magnesium hydroxide, magnesium carbonate, magnesium calcium carbonate, calcium carbonate, aluminum hydroxide, calcium oxalate, calcium phosphate, aluminum metaphosphate, sodium zinc potassium polyphosphate glass, and sodium calcium magnesium polyphosphate glass..

5. The method of any of the preceding claims wherein the solid acid-precursor is

20   coated with a hydrolysis-delaying material.

6. The method of any of the preceding claims wherein the fluid further comprises a water-soluble agent that accelerates hydrolysis of the solid acid-precursor.

7. The method of claim 6 wherein the agent is selected from the group consisting of esters, diesters, anhydrides, lactones, alkali metal alkoxides, alkali metal

hydroxides, carbonates, bicarbonates, alcohols, propylene glycol diacetate, ammonium hydroxide, amides, amines, alkanol amines and mixtures thereof.

8. The method of any of the preceding claims wherein the fluid further comprises an acid.

5   9. The method of claim 8 wherein the acid is selected from the group consisting of hydrochloric acid, hydrofluoric acid, ammonium bifluoride, formic acid, acetic acid, lactic acid, glycolic acid, aminopolycarboxylic acids, polyaminopolycarboxylic acids, salts thereof and mixtures thereof.

10. The method of any of the preceding claims wherein the fluid further comprises

10   one or more than one of a viscosifier and a proppant.

11. A method of accelerating the release of acid from a solid acid-precursor comprising mixing a solid acid-reactive material with said solid acid-precursor and contacting said mixture with an aqueous fluid.
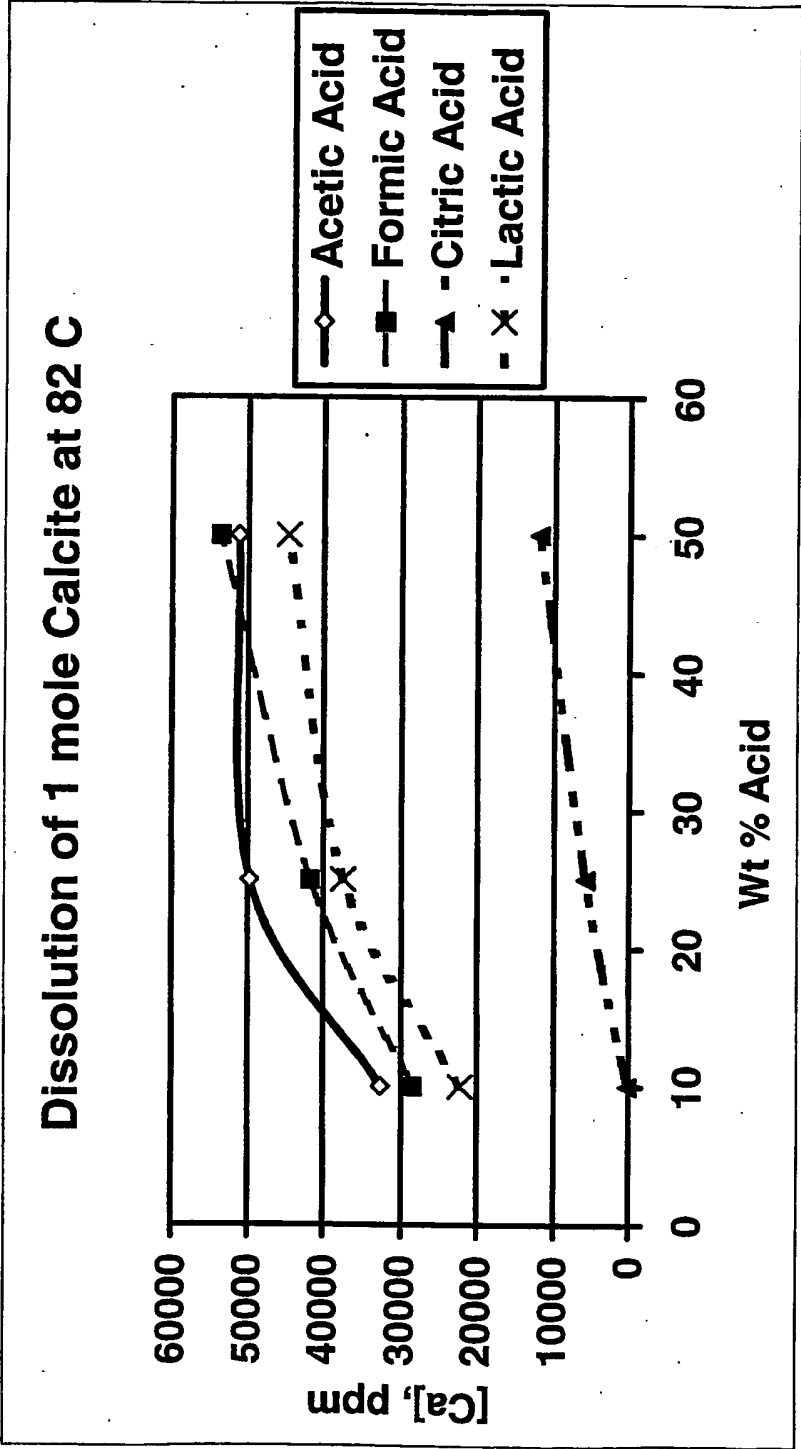
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FIG. 1

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   E21B43/27

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 401 431 A (CONOCO INC ; DU PONT (US)) 12 December 1990 (1990-12-12) page 2, line 50 - page 3, line 23 page 4, line 41 - line 54; claims 1,3	1,2
Y	US 3 630 285 A (CLAYTOR EDWIN E JR ET AL) 28 December 1971 (1971-12-28) column 1, line 19 - line 44 column 2, line 21 - column 3, line 6 column 3, line 50 - line 70 claims 1-10	1,2,6-9
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A	column 4, line 34 - line 68	10

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

° Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

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'P' document published prior to the international filing date but later than the priority date claimed

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'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 February 2004	24/02/2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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